

Statistical Thermodynamics in Chemistry and Biology

10. The Boltzmann distribution law

Per-Olof Åstrand

D3-119 Realfagsbygget, Department of Chemistry,
Norwegian University of Science and Technology,
per-olof.aastrand@ntnu.no

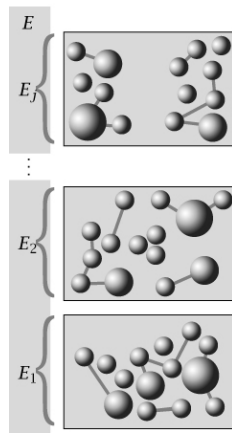
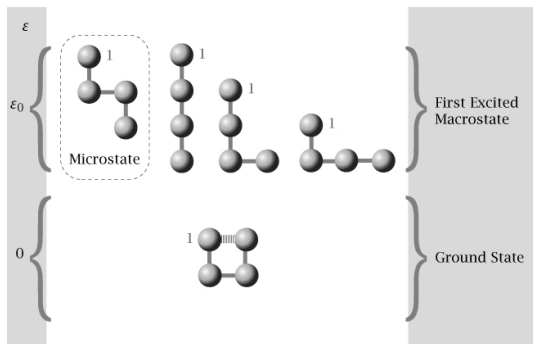
March 14, 2017

Probability distributions for atoms and molecules

Today's agenda

- ▶ The Boltzmann distribution law (slightly different from chapter 5)
- ▶ Partition functions
- ▶ Thermodynamic properties from partition functions

Typical example



Derivation of the Boltzmann distribution law

- ▶ System of N particles with discrete energy levels, $E_j, j = 1, 2, \dots, t$
- ▶ Aim at calculation of the probability, p_j , to be in each state j .
- ▶ Minimize Helmholtz free energy in the form,

$$dF = dU - TdS = 0$$

(previous derivation in chapter 5: maximizing the entropy, $dS = 0$)

- ▶ Express the entropy in terms of probabilities:

$$S = -k_B \sum_{j=1}^t p_j \ln p_j$$

and

$$dS = -k_B \sum_{j=1}^t (1 + \ln p_j) dp_j$$

Derivation of the Boltzmann distribution law

Part 2

- ▶ We postulate that the macroscopic internal energy U is (the average of) the microscopic energy

$$U = \sum_{j=1}^t p_j E_j$$

$$dU = \sum_{j=1}^t (E_j dp_j + p_j dE_j)$$

- ▶ From quantum mechanics:
 - ▶ Heat does not change the energy levels (but work does).
 - ▶ Heat changes the populations (probabilities to be in each level): dp_j
- ▶ We do not want modify the energy levels, just find the optimum p_j (constant V and N):

$$dU = \sum_{j=1}^t E_j dp_j$$

Derivation of the Boltzmann distribution law

Part 3

- ▶ We want to minimize F ,

$$dF = dU - TdS = 0$$

with the constraint that the probabilities, p_j , always sum up 1. The constraint is expressed with a Lagrange multiplier, α , as

$$\alpha \sum_{j=1}^t dp_j = 0$$

- ▶ We thus get

$$dF = \sum_{j=1}^t (E_j + k_B T (1 + \ln p_j) + \alpha) dp_j = 0$$

- ▶ It has to be 0 for each value of j ,

$$\ln p_j = -\frac{E_j}{k_B T} - \frac{\alpha}{k_B T} - 1$$

- ▶ (Note that the book uses the notation p_j^* for p_j when the condition $dF = 0$ is fulfilled. I use p_j everywhere.)

Derivation of the Boltzmann distribution law

Part 4

- ▶ Exponentiate

$$p_j = e^{-\frac{E_j}{k_B T}} e^{-\frac{\alpha}{k_B T} - 1}$$

- ▶ We need to eliminate α . Rewrite

$$\sum_{j=1}^t p_j = 1 \quad \text{as} \quad 1 = \sum_{j=1}^t e^{-\frac{E_j}{k_B T}} e^{-\frac{\alpha}{k_B T} - 1}$$

and divide p_j by “1” to get the **Boltzmann distribution law**

$$p_j = \frac{p_j}{1} = \frac{e^{-\frac{E_j}{k_B T}}}{\sum_{j=1}^t e^{-\frac{E_j}{k_B T}}} = \frac{e^{-\frac{E_j}{k_B T}}}{Q}$$

where Q is the **partition function**.

Derivation of the Boltzmann distribution law

Part 5

- ▶ The **partition function** is thus defined as

$$Q = \sum_{j=1}^t e^{-\frac{E_j}{k_B T}}$$

and is in principle impossible to obtain for large and complex systems (too many states j).

- ▶ We note that the **relative probability** between two states i and j is

$$\frac{p_i}{p_j} = \frac{\frac{e^{-\frac{E_i}{k_B T}}}{Q}}{\frac{e^{-\frac{E_j}{k_B T}}}{Q}} = e^{\frac{-(E_i - E_j)}{k_B T}}$$

- ▶ Note: more particles will have low energies and fewer particles will have higher energies
- ▶ Example: Constant total energy: there are many more arrangements (larger multiplicity) when many particles have relatively small energies than if a few particles have high energies.

Ex. 10.2. The Maxwell-Boltzmann distribution of velocities

- Kinetic gas theory: classical mechanics for the kinetic energy, ε ,

$$\varepsilon(v) = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

- According to Boltzmann's distribution law, the probability $p(v_x)$ is

$$p(v_x) = \frac{e^{-\frac{\varepsilon(v_x)}{k_B T}}}{\int_{-\infty}^{\infty} e^{-\frac{\varepsilon(v_x)}{k_B T}} dv_x} = \frac{e^{-\frac{mv_x^2}{2k_B T}}}{\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x} = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2k_B T}}$$

which is called the **Maxwell-Boltzmann distribution**. We have used (from Appendix D)

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

Ex. 10.2. The Maxwell-Boltzmann distribution

Part 2

- ▶ The *mean square velocity* $\langle v^2 \rangle$ may be obtained,

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 p(v_x) dv_x = \left(\frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} v_x^2 e^{-\frac{mv_x^2}{2k_B T}} dv_x$$

- ▶ Again use Appendix D (and $\int_{-\infty}^{\infty} = 2 \int_0^{\infty}$ for this integral):

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

- ▶ We get

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \quad \Rightarrow \quad \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} k_B T$$

Ex. 10.2. The Maxwell-Boltzmann distribution

Part 3

► Generalize to three dimensions:

- Since $v^2 = v_x^2 + v_y^2 + v_z^2$ and for an ideal gas $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T$$

i.e. the average kinetic energy has a contribution of $\frac{3}{2}k_B T$ per particle. Note the close relation between kinetic energy and temperature.

- Since the velocity components are independent,

$$p(v) = p(v_x)p(v_y)p(v_z) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_B T}}$$

What does the partition function tell us?

- ▶ It is a **sum** of *Boltzmann factors*

$$e^{-\frac{E_j}{k_B T}}$$

- ▶ In many cases, $E_1 = 0$,

$$Q = \sum_{j=1}^t e^{-\frac{E_j}{k_B T}} = 1 + e^{-\frac{E_2}{k_B T}} + e^{-\frac{E_3}{k_B T}} + \dots + e^{-\frac{E_t}{k_B T}}$$

- ▶ $E_j \rightarrow 0$ or $T \rightarrow \infty$

$$\frac{E_j}{k_B T} \rightarrow 0 \Rightarrow p_j \rightarrow \frac{1}{t} \Rightarrow Q \rightarrow t$$

- ▶ $E_j \rightarrow \infty$ or $T \rightarrow 0$

$$\frac{E_j}{k_B T} \rightarrow \infty \Rightarrow (p_1 \rightarrow 1, p_{j \neq 1} \rightarrow 0) \Rightarrow Q \rightarrow 1$$

Density of states

- ▶ In some cases the energy states are **degenerate**, i.e. different states have the same energy.
- ▶ We can then sum over all *macrostates*, i.e. states with distinct energy, and take the degeneracy into account explicitly.

$$Q = \sum_{n=1}^{n_{\max}} W(E_n) e^{-\frac{E_n}{k_B T}}$$

where $W(E_n)$ is the **density of states** or **degeneracy**.

- ▶ Alternatively, the density of states, $W(E_n)$, is the number of states in the interval $E_n - \delta \leq E_n \leq E_n + \delta$, where δ is a small number.

Distinguishable or indistinguishable particles

- Consider first distinguishable particles (A and B):

$$E_j = \varepsilon_m^A + \varepsilon_n^B$$

$$q_A = \sum_{m=1}^a e^{-\frac{\varepsilon_m^A}{k_B T}}; \quad q_B = \sum_{n=1}^b e^{-\frac{\varepsilon_n^B}{k_B T}}$$

- We would like to express Q in q_A and q_B ,

$$\begin{aligned} Q &= \sum_{j=1}^t e^{-\frac{E_j}{k_B T}} = \sum_{m=1}^a \sum_{n=1}^b e^{-\frac{\varepsilon_m^A + \varepsilon_n^B}{k_B T}} = \sum_{m=1}^a \sum_{n=1}^b e^{-\frac{\varepsilon_m^A}{k_B T}} e^{-\frac{\varepsilon_n^B}{k_B T}} \\ &= \left(\sum_{m=1}^a e^{-\frac{\varepsilon_m^A}{k_B T}} \right) \left(\sum_{n=1}^b e^{-\frac{\varepsilon_n^B}{k_B T}} \right) = q_A q_B \end{aligned}$$

- In general for N particles: $Q = q^N$
- For indistinguishable particles, we cannot see the difference between $q_A q_B$ and $q_B q_A$

$$Q = \frac{q^N}{N!}$$

Thermodynamic properties from partition functions

The internal energy, U , from the partition function

- ▶ The internal energy as an average over states,

$$U = \sum_{j=1}^t p_j E_j = Q^{-1} \sum_{j=1}^t E_j e^{-\beta E_j}$$

where $\beta = \frac{1}{k_B T}$.

- ▶ Note that

$$\left(\frac{\partial Q}{\partial \beta} \right) = \frac{\partial}{\partial \beta} \sum_{j=1}^t e^{-\beta E_j} = - \sum_{j=1}^t E_j e^{-\beta E_j}$$

- ▶ U is thus obtained as

$$U = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right) = - \left(\frac{\partial \ln Q}{\partial \beta} \right)$$

and we have expressed U only in terms of the partition function Q and other macroscopic properties (in this case T).

The internal energy, U , from the partition function

Part 2

- ▶ Since $\beta = \frac{1}{k_B T}$,

$$\left(\frac{\partial \beta}{\partial T} \right) = -\frac{1}{k_B T^2}$$

such that

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

- ▶ The average particle energy for **indistinguishable** particles, $Q = q^N / N!$,

$$\langle \varepsilon \rangle = \frac{U}{N} = \frac{k_B T^2}{N} \left(\frac{\partial \ln q^N}{\partial T} \right) + 0 = k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right) = - \left(\frac{\partial \ln q}{\partial \beta} \right)$$

- ▶ Where did the $N!$ term go? What is $\langle \varepsilon \rangle$ for distinguishable particles?

The entropy from the partition function

- ▶ The definition of the entropy in terms of probabilities is

$$S = -k_B \sum_{j=1}^t p_j \ln p_j$$

- ▶ Substituting the Boltzmann distribution law,

$$p_j = Q^{-1} e^{-\frac{E_j}{k_B T}}$$

gives

$$\begin{aligned} S &= -k_B \sum_{j=1}^t \left(Q^{-1} e^{-\frac{E_j}{k_B T}} \right) \left(\ln \left(\frac{1}{Q} \right) - \frac{E_j}{k_B T} \right) \\ &= k_B \ln Q \sum_{j=1}^t p_j + \frac{1}{T} \sum_{j=1}^t p_j E_j = k_B \ln Q + \frac{U}{T} = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right) \end{aligned}$$

where

$$\sum_{j=1}^t p_j = 1 ; \quad U = \langle E \rangle = Q^{-1} \sum_{j=1}^t E_j e^{-\frac{E_j}{k_B T}}$$

More thermodynamic properties from the partition function

Constant (T, V, N)

Use regular thermodynamics to get more properties:

Internal energy: $U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$

Entropy: $S = k_B \ln Q + \frac{U}{T}$

Helmholtz free energy: $F = U - TS = -k_B T \ln Q$

Chemical potential: $\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \left(\frac{\partial \ln Q}{\partial N} \right)_{T,V}$

Pressure: $p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$

Ex. 10.5. The Schottky two-state model

- ▶ **System:** N distinguishable particles with two energy levels for each particle, 0 and $\varepsilon_0 > 0$
- ▶ Useful for many different problems,
 - ▶ Dimer or polymer lattice models (Ex. 8.1 and Ex. 8.2)
 - ▶ Atoms or molecules excited by electromagnetic radiation.
 - ▶ Behavior of spins in magnetic fields (Ex. 10.6)

but here we keep it general.

- ▶ Find the average particle energy, $\langle \varepsilon \rangle$, the heat capacity, C_V , the entropy and the free energy per particle from the partition function.
- ▶ The particle partition function, q ,

$$q = 1 + e^{-\beta \varepsilon_0}$$

Ex. 10.5. The Schottky two-state model

Part 2

- ▶ The energy per particle is given as

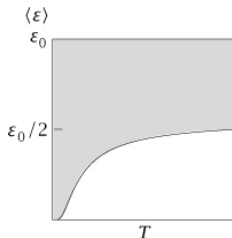
$$\langle \varepsilon \rangle = -\frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right) = \frac{\varepsilon_0 e^{-\beta \varepsilon_0}}{1 + e^{-\beta \varepsilon_0}}$$

as shown in the top figure as a function of temperature. Note that $\langle \varepsilon \rangle \rightarrow \frac{\varepsilon_0}{2}$ when $T \rightarrow \infty$.

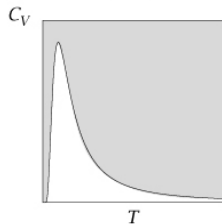
- ▶ For the heat capacity, C_V , use its definition $C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}$ and $U = N\langle \varepsilon \rangle$,

$$\begin{aligned} C_V &= N \left(\frac{\partial \langle \varepsilon \rangle}{\partial T} \right)_{V,N} = N \left(\frac{\partial \langle \varepsilon \rangle}{\partial \beta} \right)_{V,N} \left(\frac{\partial \beta}{\partial T} \right) \\ &= -\frac{N}{k_B T^2} \left(\frac{\partial \langle \varepsilon \rangle}{\partial \beta} \right)_{V,N} \end{aligned}$$

(a) Average Energy



(b) Heat Capacity



Ex. 10.5. The Schottky two-state model

Part 3

- Note that $d\left(\frac{u}{v}\right) = \frac{vu' - uv'}{v^2}$, to get

$$\begin{aligned}\left(\frac{\partial \langle \varepsilon \rangle}{\partial \beta}\right)_{V,N} &= \frac{(1 + e^{-\beta \varepsilon_0})(-\varepsilon_0^2 e^{-\beta \varepsilon_0}) - (\varepsilon_0 e^{-\beta \varepsilon_0})(-\varepsilon_0 e^{-\beta \varepsilon_0})}{(1 + e^{-\beta \varepsilon_0})^2} \\ &= \frac{-\varepsilon_0^2 e^{-\beta \varepsilon_0}}{(1 + e^{-\beta \varepsilon_0})^2}\end{aligned}$$

which gives

$$C_V = \frac{N \varepsilon_0^2}{k_B T^2} \frac{e^{-\beta \varepsilon_0}}{(1 + e^{-\beta \varepsilon_0})^2}$$

which is also shown as a function of the temperature on the previous slide.

Ex. 10.5. The Schottky two-state model

Part 4

- ▶ The entropy is given as

$$S = \frac{U}{T} + k_B \ln Q = \frac{N\varepsilon_0 e^{-\beta\varepsilon_0}}{T(1 + e^{-\beta\varepsilon_0})} + k_B N \ln (1 + e^{-\beta\varepsilon_0})$$

- ▶ and Helmholtz free energy as

$$F = -k_B T \ln Q = -Nk_B T \ln q = -Nk_B T \ln (1 + e^{-\beta\varepsilon_0})$$

Summary

- ▶ Derived the **Boltzmann distribution law** for the canonical ensemble
- ▶ Defined the corresponding **partition function**.
- ▶ Divided the partition function into particle contributions: $Q = \frac{q^N}{N!}$ (for indistinguishable particles).
- ▶ Connected thermodynamic properties to the partition function.

Exam June 2012 - Exercise 1

Boltzmann distribution law

a) How is an *ensemble* defined in statistical thermodynamics? Discuss briefly the differences between the *microcanonical*, *canonical* and *isobaric-isothermal* ensembles. Which are the variables, fundamental function and extremum principle for each ensemble, respectively? Which ensembles are preferred experimentally (motivate the answer)?

b) For which ensemble is the Boltzmann distribution,

$$p_j = \frac{g_j e^{-E_j/k_B T}}{Q} \quad (1)$$

derived? What is g_j (we have also used the notation W_j) in eq. (1)? How is Q defined? What does the magnitude of Q tell us?

c) Assume that we have three molecules, $N = 3$, and also assume that only the two lowest molecular states, $\varepsilon_0 = \varepsilon$ and $\varepsilon_1 = 2\varepsilon$, can be occupied. What is the probability for that the total energy, E , is 5ε ? The temperature, $T = 300$ K and $\varepsilon = 10$ kJ/mol.

Exam June 2012 - Exercise 1

Part 2 - to be solved when we introduced K and x

Boltzmann distribution law

d) The equilibrium constant, K ,

$$K = \frac{x_1}{x_2}$$

is investigated. Show that it can be written both in terms of the energy difference, $\Delta E = E_1 - E_2$, as

$$K = Ae^{-\Delta E/k_B T}$$

and in terms of the Helmholtz free energy difference, $\Delta F = F_1 - F_2$, as

$$K = e^{-\Delta F/k_B T}$$

Use eq. (1) as a starting point. Define A in terms of properties used in eq. (1).